

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification : Not classified	A2	(11) International Publication Number: WO 97/19582 (43) International Publication Date: 5 June 1997 (05.06.97)
(21) International Application Number: PCT/US96/18507 (22) International Filing Date: 18 November 1996 (18.11.96) (30) Priority Data: 08/559,006 16 November 1995 (16.11.95) US (71) Applicant: H.B. FULLER LICENSING & FINANCING, INC. [US/US]; 1200 Willow Lake Boulevard, St. Paul, MN 55110-5132 (US). (72) Inventors: SIMMONS, Eugene; 3440 Montmorency Street, Vadnais Heights, MN 55110 (US). SWEENEY, Kevin; 338 Wedgewood Drive, Mahtomedi, MN 55115 (US). LINDQUIST, Jeffrey; 9646 Indian Boulevard, Cottage Grove, MN 55016 (US). OLSON, Christopher; 5154 Parkside Drive, Paducah, KY 42001 (US). CARTES, Freddie; 1020 Wayside Drive, Paducah, KY 42003 (US). FARMER, James; 602 Newton, Johnston, IL 62951 (US). (74) Agents: STEINKRAUS, Walter, J. et al.; 1540 Kinnard Financial Center, 920 Second Avenue South, Minneapolis, MN 55402 (US).	(81) Designated States: AU, BR, CA, CN, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>Without international search report and to be republished upon receipt of that report.</i>	
(54) Title: A POLYMERIC COMPOSITION IN PELLET FORM		
(57) Abstract A polymeric composition in pellet form comprising a tacky hot melt composition, comprising a) from about 5 % by weight to about 90 % by weight of a thermoplastic polymer, b) from about 10 % by weight to about 65 % by weight of a tackifying resin, c) up to about 50 % by weight of a plasticizer, d) up to about 2 % by weight of an antioxidant, and a pelletizing aid, wherein the tacky hot melt composition is a pressure sensitive adhesive having a storage modulus, G', at about 25 °C, of less than about 5 x 10 ⁶ dynes/cm ² , and each pellet has a substantially tack-free surface. This invention further discloses a polymeric composition in pellet form suitable for molding articles. The composition comprises a tacky hot melt composition comprising at least one high molecular weight triblock copolymer of the general configuration A-B-A and a plasticizer and a pelletizing aid. The pelletizing aid substantially surrounds the tacky composition such that the molded articles are substantially free from surface tack. A method of forming the pellets is also disclosed.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

A POLYMERIC COMPOSITION IN PELLET FORM

Field Of The Invention

This invention relates to a polymeric composition in pellet form comprising a tacky hot melt composition which can be used either for hot melt pressure sensitive applications or for molded articles. Those compositions suitable for pressure sensitive applications are defined by having a storage modulus, G' , at 25°C, of less than about 5×10^6 dynes/cm², and each pellet has a substantially tack-free surface prior to melting, and pressure sensitive characteristics after resolidification. The polymeric compositions suitable for use in injection molding preferably comprise a high molecular weight block copolymer and have a tack-free surface both prior to melting the pellets, and after melting and resolidification.

Background Of The Invention

Tacky hot melt compositions have been used widely in the adhesive industry for a wide range of applications such as for pressure sensitive adhesives due to their ability to adhere to a wide variety of substrates. A primary property of a hot melt pressure sensitive composition is that it remain tacky at room temperature so that it may be adhered to substrates when it has completely cooled from its molten state. Examples of applications which require this property are tape and label applications. Paper, polyethylene, polypropylene or other such substrates may be coated with the tacky hot melt composition, covered with release liner, and then shipped this way for later applications such as for labels used on various containers, books, magazines, or envelopes just to name a few.

The use of tacky hot melt compositions in other applications has been precluded by the fact that they remain tacky. Yet it may be desirable to use these soft and very flexible compositions for other applications. One such application

is the formation of articles by injection molding. Some articles formed by injection molding include shoe soles, drum pads, therapeutic hand exercising grips, shock absorbers, acoustical insulators, chair pads and imitation skin for use in the entertainment industry but this list is not exhaustive.

5 The tackiness exhibited by these hot melt pressure sensitive adhesives also makes them difficult to handle. They may adhere to skin, clothing, application equipment, floors, or other places that are undesirable. Many packaging methods have been devised to avoid the problems encountered in the handling of these hot melt pressure sensitive compositions.

10 Hot melt adhesives are supplied as pellets, pillows as disclosed by German Pat. 22 48 046, slats or chicklets, blocks, and cakes.

A further problem encountered with hot melt pressure sensitive adhesives is that the tackiness may result in blocking individual pieces together resulting in a large mass in the shipping containers. This makes it difficult to get the adhesive
15 into many different types of hot melt premelter tanks used in the industry.

U.S. Pat. No. 3,723,035 discloses a machine performing an improved method of packaging a hot melt adhesive. This produces an end product known as pillows to one of skill in the art. These pillows can be coextruded with a non-tacky polymer such as polyethylene for producing pressure sensitive adhesives
20 that are tacky at room temperature. This coextrusion coating prevents the pillows from blocking together in a solid mass at room temperature. Using this method, once the coextruded pillows are melted for use on an application line, the hot melt composition again becomes tacky when it returns to room temperature.

French Pat. No. 2,544,654 published Oct. 26, 1984 discloses forming a
25 tackless hot melt by adding the molten hot melt to a mold which contains a preformed support layer having a transfer film which is compatible with the hot melt.

U.S. Pat. No. issued June 12, 1988 and 4,755,245 issued July 5, 1988
disclose forming a protective coating for an adhesive material by electrostatically
30 coating a mold or cavity with a powder screen and then pouring hot melt into the mold.

French Pat. No. 2,601,616 published Oct. 22, 1988 discloses forming blocks of hot melt pressure sensitive adhesive by casting the adhesive into molds precoated by spraying with a film of non self-sticking hot melt material.

German Pat. Nos. DE 31 38 222, DE 32 34 065, and DE 36 25 358 teach
5 coating or wrapping a formed hot melt block with various types of film.

U.S. Pat. No. 5,257,491 to Rouyer et al. teaches a method of packaging a hot melt adhesive composition wherein the adhesive composition is sufficiently solidified or when flowable.

U.S. Pat. No. 5,401,455 to Hatfield et al. issued March 28, 1995 teaches a
10 method for packaging hot melt adhesive compositions comprising the use of a mold being in contact with a refrigerant gas or liquid heat sink. Hatfield teaches that when a hot melt adhesive is poured into a cavity lined with film in its molten state, the adhesive is fused to some extent with the film. According to Hatfield, this in turn allows some mixing and compatibilizing of the film, improving the
15 opportunity for more complete mixing.

U.S. Pat. No. 5,057,571 to Malcolm et al. discloses at column 8 line 59 to column 9 line 14 a method for pelletizing a preblend of a radial block copolymer and a tackifying resin. This preblend is then used to make hot melt adhesives for disposable article construction. The preblend is manufactured on an extruder.
20 The pelletized preblend was then used to make an adhesive using conventional hot melt mixers. This is a two step process of making hot melt pressure sensitive adhesives, and it was never intended to teach making a finished product in a free-flowing pellet form.

The current inventors have found a polymeric composition in a free-
25 flowing pellet form that can be either a hot melt pressure sensitive adhesive or a polymeric composition that has a surface that remains tack-free after melting and resolidification.

Summary Of The Invention

The present invention discloses a polymeric composition in pellet form, comprising:

- I. from about 97 to about 99.9 percent by weight of a tacky hot melt composition, comprising:
 - a) from about 5% to about 90% by weight of a thermoplastic polymer;
 - b) from about 0% to about 65% of a tackifying resin;
 - c) from about 0% to about 50% by weight of a plasticizer; and
 - d) up to about 2% of an antioxidant; and
- II. from about 0.1% to about 3% by weight of a pelletizing aid, wherein the composition comprises some minimum amount of tackifier or plasticizer or both.

The tacky hot melt composition is a pressure sensitive adhesive having a storage modulus, G' , at 25°C, of less than about 5×10^6 dynes/cm², as measured using a Rheometrics Scientific Dynamic Mechanical Spectrometer Model #RDS7700.

The pelletizing aid is used to provide hot melt pressure sensitive adhesives in pellet form wherein the pellet has a tack-free surface. Once the pellets are melted and resolidified, these compositions once again return to their original tacky state. These pellets are free-flowing and the resultant pelletized composition can be used in various tape and label applications, in non-woven applications where pressure sensitive adhesives are used such as for positioning of feminine napkins, diaper fastening systems, and disposable article construction, in the automotive industry where hot melt pressure sensitive adhesives are used for assembly applications, and for medical applications.

The present invention further discloses a polymeric composition in pellet form, comprising:

- I. from about 97 to about 99.9 percent by weight of a tacky hot melt composition, comprising:

- a) from about 2.0 to about 20 percent by weight of a block copolymer having the general configuration A-B-A and a molecular weight greater than about 200,000;
- b) from about 20 to about 98 percent by weight of a compatible plasticizer; and
- 5 c) from about 0% to about 30 percent by weight of a compatible block copolymer;
- II. from about 0.1% to about 3 percent by weight of a pelletizing aid.

The resultant polymeric compositions have a tack-free surface both prior to
10 melting the pellets, and after melting and resolidification.

The resultant tacky hot melt compositions are characterized by a specific gravity of greater than about 0.8, Mettler Softening Points of greater than about 90°C and Bloom Gelometer readings of greater than about 20 grams.

The pellets thus formed are soft, non-blocking, substantially without
15 surface tack and exhibit an elastic rebound, as characterized by G' (elastic or storage modulus) measurements. These compositions are suitable for use in molding, especially injection molding. Any molded products produced therefrom also retain the substantially tack-free surface. While the bulk composition determines the properties of the pellets, the pelletizing aid determine the surface
20 properties of the pellets, and has no effect on the bulk properties.

These pellets are suitable for use in molding, especially injection molding. The composition suitable for such processes comprises:

- I. A tacky hot melt composition, comprising:
- a) at least one high molecular weight triblock copolymer of
25 the general configuration A-B-A; and
- b) a plasticizer; and
- II. A pelletizing aid,

wherein said pelletizing aid substantially surrounds the tacky composition such that the molded articles are soft, non-blocking and have a substantially tack-free
30 surface. Optionally, other compatible block copolymers such as radial blocks and diblocks and other triblocks can be added. Preferably, the tacky hot melt

composition comprises from about 97 to about 99.9 percent by weight of the article, more preferably from about 99 to about 99.9 percent by weight.

Any molded articles produced therefrom also retain the substantially tack-free surface and rebound properties. Such articles can include drum pads useful as
5 acoustical pads for vibration damping, disc players, ear phones, percussion surfaces on electronic drum kits and so on; soles, shoes insoles, in-line skate soles and so on; pads for use in athletic gear such as mouth pads, protective guards, encapsulants for other solid protective pads and so on; bicycle seats, gloves, bicycle shorts and so on; medical equipment such as pads for wheel chairs, donut-
10 shaped pads for seats and so on; furniture pads such as mattress pads, chair pads and so on; special effects articles such as body parts, Santa Claus' bellies, synthetic skin, and others that are useful in movies; and bandages, especially for burn wounds. While the rest of the composition determines the overall bulk properties of the pellets and articles molded therefrom, the pelletizing aid
15 determines the surface properties of not only the pellets, but the articles made from such pellets.

The present invention also discloses an under-water pelletizing process for making the tacky hot melt compositions in pellet form, utilizing a pelletizing aid to produce pellets that have a substantially tack-free surface making them non-
20 blocking, and are soft. The process varies slightly for each product, dependent mainly on the plasticizer loading, and comprises the steps of:

- a) blending the hot melt components to form a substantially homogeneous hot melt mixture;
- b) forcing said substantially homogeneous hot melt mixture through a
25 die for forming substantially homogeneous hot melt ribbons and forming resultant pellets therefrom;
- c) solidifying said pellets by use of a cooling medium; and
- d) applying said pelletizing aid at some point during the pelletizing process.

30 The pellets can be made into any convenient size. Preferably, the pellets are substantially spherical, with sizes ranging from about 1/8 to about 3/8 inch (about 3mm to about 10mm) in diameter for easy handling. The pellets can also

be ellipsoidal and cylindrical. The preferred dimensions for these shapes can range from about 3mm to about 10mm to about 10mm by 20mm.

Detailed Descriptions Of The Preferred Embodiments

5 The pelletized polymeric compositions of the present invention can exhibit a spectrum of properties, ranging from compositions having hot melt pressure sensitive adhesive properties to compositions suitable for molding non-tacky articles. Those polymeric compositions for use in pressure sensitive applications have a storage modulus, G' , at 25°C of less than about 5×10^6 dynes/cm², and
10 preferably have a storage modulus, G' , at about 25°C, from about 1×10^4 to about 5×10^6 dynes/cm² while those useful for molding applications can have a storage modulus of greater than about 5×10^6 dynes/cm². The storage modulus, G' , is measured using a Rheometrics Scientific Dynamic Mechanical Spectrometer Model #RDS7700.

15 The thermoplastic polymers useful for the present invention can include A-B-A triblock copolymers, A-B diblock copolymers, A-B-A-B-A-B multiblock copolymers, radial block copolymers and grafted versions thereof; homopolymers, copolymers and terpolymers of ethylene; and homopolymers, copolymers and terpolymers of propylene; and mixtures thereof. Radial block copolymers include
20 Y-block and star polymers as well as other configurations. The A-B-A block copolymers useful herein are those described in U.S. Pat. No. 4,136,699 to (Collins et al.), incorporated herein by reference, issued January 30, 1979. Examples include those polymers available under the Kraton™ G series from Shell Chemical Co. in Houston, TX. There are various grades available including
25 Kraton™ G-1726, Kraton™ G-1650, Kraton™ G-1651, Kraton™ G-1652, Kraton™ G-1657, all saturated A-B diblock/A-B-A triblock mixtures with ethylene/butylene midblocks; Kraton™ D-1112 a high percent A-B diblock linear styrene-isoprene-styrene polymer; Kraton™ D-1107 and Kraton™ D-1111, primarily A-B-A triblock linear styrene-isoprene-styrene block copolymers;
30 Kraton D4433X, a linear SIS block copolymer with an oil content of 30% by weight and Kraton D1184, a high molecular weight SBS block copolymer both available from Shell Chemical Co.; Stereon™ 840A and Stereon™ 841A. A-B-A-

B-A-B multiblock SBS block copolymers available from Firestone in Akron, Ohio; Europrene™ Sol T-193B, a linear SIS block copolymer available from Enichem Elastomers in New York, NY; Europrene™ Sol T-190, a linear styrene-isoprene-styrene block copolymer and Europrene™ Sol T-163, a radial SBS block copolymer both also available from Enichem Elastomers; Vector™ 4461-D, a linear SBS block copolymer available from Exxon Chemical Co. in Houston, Texas; Vector™ 4111, 4211 and 4411, fully coupled linear SIS block copolymers containing different weight percentages of styrene endblock; and Vector™ 4113, a highly coupled linear SIS block copolymer also available from Exxon Chemical Co.; and DPX-550, DPX-551 and DPX-552 radial SIS block copolymers available from Dexco Polymers in Houston, Texas. This list is not exclusive and there are numerous grades of block copolymers available from various sources for hot melt pressure sensitive adhesives. These polymers may be used alone, or in any combinations. These polymers are useful from about 5% to about 90% by weight in the polymeric composition.

The polymeric compositions suitable for molding applications may comprise any of the above mentioned polymers which have a high molecular weight and preferably have a weight average molecular weight greater than about 200,000 as measured by Gel Permeation Chromatography, with values reported relative to styrene standards. The polymer is preferably a substantially linear copolymer having the general configuration A-B-A, wherein the A block can be polystyrene and the B block can be ethylene-butylene, ethylene-propylene, isoprene, butadiene or mixtures thereof, and preferably the B block is ethylene-butylene or ethylene-propylene. Polymers of this type, such as Kraton™ G-1651, are twice the molecular weight of conventional styrene-ethylene/butylene-styrene (S-EB-S) block copolymers used in the hot melt adhesive industry. This copolymer is present in amounts from about 2 to about 20 percent by weight and preferably from about 5 to about 20 percent by weight in the polymeric composition.

Other lower molecular weight block copolymers may be utilized with these high molecular weight block copolymers. Some examples are A-B-A triblock copolymers, A-B diblock copolymers, A-B-A-B-A-B multiblock copolymers,

radial block copolymers, and grafted versions of such copolymers including Shell Chemical's TKG-101 and RP-6912. Such A-B-A block copolymers are disclosed in Collins et al., U.S. Pat. No. 4,136,699. Some of these block copolymers are commercially available from Shell Chemical Co. under the Kraton™ G series
5 which are S-EB-S block copolymers.

Other useful polymers include atactic polyalphaolefins such as those available from Rexene Products Co. in Dallas, Texas under the tradename of Rextac™ such as RT-2280 and RT-2315 and RT-2585 having various amounts of ethylene and homogeneous linear or substantially linear interpolymers of ethylene
10 with at least one C₂ to C₂₀ alphaolefin, further characterized by each said interpolymer having a polydispersity less than about 2.5 including such polymers as Exact™ 5008, an ethylene-butene copolymer, Exxpol SLP-0394™, and ethylene-propylene copolymer, Exact™ 3031, an ethylene-hexene copolymer, all available from Dow Chemical Co. in Midland, MI. These polymers may have to
15 be used in small concentrations if utilized with such block copolymers as Kraton™ G-1651 to maintain compatibility without phase separation or snotty, gel-like compositions. These concentrations may be as low as 5% by weight in the composition.

Other compatible polymers may be useful in the polymeric compositions
20 of the present invention including ethylene vinyl acetate copolymers such as Elvax™ 410, a 14% vinyl acetate/400 melt index copolymer and Elvax™ 210, a 28% vinyl acetate/400 melt index copolymer, both available from DuPont Chemical Co. in Wilmington, DE; Escorene™ UL 7505 an ethylene vinyl acetate copolymer available from Exxon Chemical Co.; Ultrathene™ UE 64904 available
25 from Quantum Chemical Co., U.S.I. Division in Cincinnati, OH; and AT 1850M available from AT Polymers & Film Co. in Charlotte, North Carolina. Copolymers of ethylene and methyl acrylate (methacrylates as well as acrylates) are also useful including Optema™ TC-140, XS-93.04 and TC-221 available from Exxon Chemical Co.; Lotryl™ 28 MA 175 and 35 MA 05 1000 available from Elf
30 Atochem North America in Philadelphia, PA. Ethylene methyl acrylate copolymers are also available from Chevron under the tradename of Emac™ and from Quantum Chemical Co. under the tradename of Acrythene™. Copolymers

of ethylene and n-butyl acrylate are also useful in the adhesives of the invention. They are available from Quantum Chemical Co. under the tradename of Enathene™ including EA80808, EA 89821 and EA89822; from Elf Atochem North America under the tradename of Lotryl™ including 35 BA 900 and 35 BA 5 1000; from Exxon Chemical Co. under the tradename of Escorene™ including XW-23.AH and XW-22. These polymers may also have to be used in small concentrations with some of the block copolymers such as Kraton™ G-1651.

The polymeric compositions may also comprise a tackifying resin. While they are preferable for use in hot melt pressure sensitive compositions, they may 10 or may not be utilized in the molded article compositions. The tackifying resins useful herein include aliphatic, cycloaliphatic and aromatic hydrocarbons and modified hydrocarbons and hydrogenated derivatives; terpenes and modified terpenes and hydrogenated derivatives; rosins and modified rosins and hydrogenated derivatives; and mixtures thereof. These tackifying resins have a 15 ring and ball softening point of between about 70°C and 150°C. They are also available with differing levels of hydrogenation, or saturation which is another commonly used term. Useful examples include Eastotac™ H-100, H-115 and H-130 from Eastman Chemical Co. in Kingsport, TN which are partially hydrogenated cycloaliphatic petroleum hydrocarbon resins with different 20 softening points. These are available in the E grade, the R grade, the L grade and the W grade. These have differing levels of hydrogenation from least hydrogenated to most hydrogenated. The E grade has a bromine number of 15, the R grade a bromine number of 5, the L grade has a bromine number of 3 and the W grade a bromine number of 1. There is also an Eastotac™ H-142R resin 25 available. Other useful tackifying resins include Escorez 1310 LC, an aliphatic hydrocarbon resin, Escorez™ 5300 and Escorez™ 5400, partially hydrogenated cycloaliphatic petroleum hydrocarbon resins, and Escorez™ 5600, a partially hydrogenated aromatic modified petroleum hydrocarbon resin all available from Exxon Chemical Co. in Houston, TX; Wingtack™ Extra which is an aliphatic, 30 aromatic petroleum hydrocarbon resin available from Goodyear Chemical Co. in Akron, OH; Herculite™ 2100 which is a partially hydrogenated cycloaliphatic petroleum hydrocarbon resin available from Hercules in Wilmington, DE; and

Zonatac™ 105 Lite which is a styrenated terpene resin made from d-limonene and available from Arizona Chemical Co. in Panama City, FL. There are numerous types of rosins and modified rosins available with differing levels of hydrogenation including gum rosins, wood rosins, tall-oil rosins, distilled rosins, 5 dimerized rosins and polymerized rosins. Some specific modified rosins include glycerol and pentaerythritol esters of wood rosins and tall-oil rosins. Commercially available grades include, but are not limited to, Sylvatac™ 1103, a pentaerythritol rosin ester available from Arizona Chemical Co., Unitac™ R-100 Lite a pentaerythritol rosin ester from Union Camp in Wayne, NJ, Zonester™ 10 100, a glycerol ester of tall oil rosin from Arizona Chemical Co., Permalyn™ 305, a pentaerythritol modified wood rosin available from Hercules, Inc. in Wilmington, DE and Foral™ 105, which is a highly hydrogenated pentaerythritol rosin ester available. Sylvatac™ R-85 which is an 85°C melt point rosin acid and Sylvatac™ 295 which is a 95°C melt point rosin acid are both available from 15 Arizona Chemical Co.. Foral™ AX is a 75°C melt point hydrogenated rosin acid available from Hercules Inc. Nirez™ V-2040 is a phenolic modified terpene resin available from Arizona Chemical Co. There are many available types and grades of tackifying resins available from many companies, and one skilled in the art would recognize that this is not an exclusive list, and that the available tackifying 20 resins are too numerous to list here. Various endblock resins are also useful in the compositions of the present invention. These include Endex™ 160, an aromatic hydrocarbon manufactured by Hercules, Inc. in Wilmington, DE; Kristalex™ 3100 and Kristalex™ 5140, alphasubstituted styrene hydrocarbons manufactured by Hercules, Inc.; and also coumarone indene resins. These tackifiers are useful from 25 about 0% to about 65% by weight, and preferably from about 10% to about 65%.

The plasticizers useful in the present invention may include mineral based oils and petroleum based oils, liquid rosins, liquid elastomers, polybutene, polyisobutylene, functionalized oils such as glycerol trihydroxyoleate and other fatty oils and mixtures thereof. A plasticizer is broadly defined as a typically 30 organic composition that can be added to the thermoplastics, rubbers and other resins to improve extrudability, flexibility, workability and stretchability in the

finished adhesive. Any material which flows at ambient temperatures and is compatible with the block copolymer may be useful.

The most commonly used plasticizers are oils which are primarily hydrocarbon oils that are low in aromatic content and are paraffinic or naphthenic in character. The oils are preferably low in volatility, transparent and have as little color and odor as possible. This invention also contemplates the use of olefin oligomers, low molecular weight polymers, vegetable oils and their derivatives and similar plasticizing oils.

Examples of useful plasticizers include Calsol™ 5120, a naphthenic petroleum based oil available from Calumet Lubricants Co. in Indianapolis, IN; Kaydol™ White Mineral Oil, a paraffinic mineral oil available from Witco Corp. in New York, NY; Parapol™ 1300, a liquid butene homopolymer available from Exxon Chemical Co. in Houston, TX; Indopol™ H-300, a liquid butene homopolymer, available from Amoco Corp. in Chicago, IL; Escorez™ 2520, a liquid aromatic petroleum based hydrocarbon resin with a pour point of 20°C, available from Exxon Chemical Co.; Regalrez™ 1018, a liquid hydrogenated aromatic hydrocarbon resin with a pour point of 18°C, available from Hercules, Inc. in Chicago, IL; and Sylvatac™ 5N, a liquid resin of modified rosin ester with a pour point of 5°C, available from Arizona Chemical Co. in Panama City, FL.

One skilled in the art would recognize that any generic 500 second or 1200 second naphthenic process oil would also be useful. These plasticizers are useful in amounts from about 0% to about 50% by weight for the hot melt pressure sensitive compositions, and up to about 98% by weight in the molded article compositions, and preferably up to about 90% by weight.

A pelletizing aid is used to change the surface characteristics of the pellets. It would be generally undesirable for molded articles manufactured by such methods as injection molding, to remain tacky. Surprisingly, a small amount of pelletizing aid can make the surface of the pellets substantially non-tacky. The pelletizing aids do not change the end use properties of the tacky composition, as in the formulas used as hot melt pressure sensitive adhesives, or they do change the physical properties of the tacky composition, as in the case of the formulas used for the molding applications.

The pelletizing aid is selected from the group consisting of polyethylene waxes, modified polyethylene waxes, polyamide waxes and stearamide waxes. Many other waxes or pelletizing aids not on this list could also be useful provided the surface of the resultant pellet is tack-free. Preferred waxes are Acrawax C™
5 stearamide wax available from Lonza, Inc. in Fairlawn, NJ; Castor™ hydroxy waxes and Paricin™ hydroxyamide waxes available from Caschem in Bayonne, NJ; Neptune™ 968 available from Shamrock Technologies in Newark, NJ; Shamrock™ S-395 polyethylene wax available from Shamrock Technologies; and
10 Hoechst™ Wax PED 121, a modified polyethylene available from Hoechst Celanese in Somerville, NJ. More preferably, these pelletizing aids are polyethylene waxes and come in powder form. The pelletizing aid is present from about 0.1 percent to about 3 percent by weight and preferably from about 0.1
15 percent to about 1 percent by weight. This amount is substantially less or comparable to the packaging film of prior art packaging methods. It is believed that the temperature of use of the tacky hot melt composition controls whether the surface of tacky hot melt composition returns to the substantially tack-free state after melting the pellets, and subsequent resolidification.

A stabilizer or antioxidant can also be used in the polymeric compositions. These compounds are added to protect the adhesive from degradation caused by
20 reaction with oxygen induced by such things as heat, light or residual catalyst from the raw materials such as the tackifying resin. Such antioxidants are commercially available from Ciba-Geigy in Hawthorne, NY and include Irganox™ 565, Irganox™ 1010 and Irganox™ 1076, all hindered phenolic antioxidants. These are primary antioxidants which act as free radical scavengers
25 and may be used alone or in combination with other antioxidants such as phosphite antioxidants like Irgafos™ 168 available from Ciba-Geigy. Phosphite antioxidants are considered secondary antioxidants, are primarily used as peroxide decomposers and are generally not used alone, but are instead used in combination with other antioxidants. Other available antioxidants are Cyanox™ LTDP, a
30 thioether antioxidant, available from Cytec Industries in Stamford, CT, Ethanox™ 330, a hindered phenolic antioxidant, available from Albemarle in Baton Rouge, LA. Many other antioxidants are available for use by themselves, or in

combination with other antioxidants. These compounds are added to the hot melts in small amounts, up to about 2% by weight in the hot melt pressure sensitive adhesive, and have no effect on the physical properties of the adhesive.

Other compounds that also could be added that have no effect on the physical properties are pigments which add color, fluorescing agents, any compounds that mask odor and fillers to mention only a few. Additives such as these are known to one of skill in the art.

Fillers come in the form of particulate matter, fibers and powders, or may be any material that does not interfere with the other components in the adhesive. Some examples include calcium carbonate, ceramics, glass, silica, quartz, mica, treated clay, titanium dioxide, boron nitrides, graphite, carbon black, metals, barium, sulfate, talc and mixtures thereof. Such additives are known to one of skill in the art.

As discussed above, the resultant pellets are soft, non-blocking, substantially free from surface tack and exhibit an elastic rebound. This last characteristic can be measured by the elastic or storage modulus, G' . The higher the modulus, the more likely that the material will return to its original shape. At lower loadings of the high molecular weight triblock copolymer, the pellets formed resemble gels. They possess some elastic rebound, but tend to retain the same physical property over a wide-temperature range, or over a long period of time. These pellets are desirable for making articles such as Santa Claus' bellies. At higher loadings of the copolymer, the pellets formed have high elastic modulus and tend to return to their original shape faster. They are more suited for producing articles such as drum pads.

Compatible polymers or copolymers discussed above can also be added to modify the properties of the pellets. These are generally of low molecular weight, and pellets made with an amount of the high molecular weight triblock copolymer tend to have more rebound than those made with the same amount of a blend of this copolymer and the low molecular weight compatible polymer or copolymer. These compatible polymers or copolymers are thus added for customizing the final applications or uses.

These pellets are suitable for use in molding, especially injection molding.

The composition suitable for such processes comprises:

- I. A tacky hot melt composition, comprising:
 - a) at least one high molecular weight triblock copolymer of
5 the general configuration A-B-A; and
 - b) a plasticizer; and
- II. A pelletizing aid;

wherein said pelletizing aid substantially surrounds the tacky composition such that the molded articles are soft, non-blocking and substantially without surface
10 tack. Optionally, other polymers such as diblock or other triblocks can be added. Preferably, the tacky hot melt composition comprises from about 97 to about 99.9 percent by weight of the article, more preferably from about 99 to about 99.9 percent by weight.

Any molded articles produced therefrom also retain the substantially tack-
15 free surface and rebound properties. Such articles can include drum pads useful as acoustical pads for vibration damping, disc players, ear phones, percussion surfaces on electronic drum kits and so on; soles shoes insoles, in-line skate soles and so on; pads for use in athletic gear such as mouth pads, protective guards, encapsulants for other solid protective pads and so on; bicycle seats, gloves,
20 bicycle shorts and so on; medical equipment such as pads for wheel chairs, donut-shaped pads for seats and so on; furniture pads such as mattress pads, chair pads and so on; special effects articles such as body parts, Santa Claus' bellies, and other that are useful in movies. Unlike the prior art, the pelletizing aid used herein blooms to the surface during the molding process, such that it substantially
25 completely surrounds the tacky composition below and produces articles substantially free of surface tack when cooled. This is surprising because the amount of pelletizing aid used in the formulation is small, and according to prior art teachings, should not substantially interfere with the properties of the bulk composition, nor should it change the surface properties.

30 The present invention further discloses a method for making such pellets for all the formulations of the invention. The manufacturing process can vary slightly for each product depending on the plasticizer loading. The current

process requires multiple passes through a co-rotating twin screw extruder with the product being pelletized at the end of each pass, and then refeed into the extruder for the further addition of plasticizer. The compositions with 90 percent plasticizer or more need three passes, while lower plasticizer loadings may require only two. It is important to note that the materials are pelletized with the pelletizing aid after both passes. The concentration of the pelletizing aid in the water can range from about 0.1 percent to about 3 percent by weight, preferably about 0.1 to about 1 percent by weight based on anticipated production rate for each pass. A specific preferred manufacturing process comprises:

- 10 a) blending the hot melt components to form a substantially homogeneous hot melt mixture;
- b) forcing said substantially homogeneous hot melt mixture through a die having a series of voids in a circular pattern to form a series of substantially homogeneous hot melt ribbons;
- 15 c) further forcing said homogeneous hot melt ribbons past rotating blades in substantially parallel position to said die, cutting said substantially homogeneous hot melt ribbons to form resultant pellets;
- d) substantially solidifying said pellets by use of a liquid cooling medium said liquid cooling medium containing a pelletizing aid, being circulated past said die and rotating blades on the side where said substantially homogeneous hot melt ribbons emerge;
- 20 e) transporting said hot melt pellets to a drying area;
- f) substantially removing liquid from said hot melt pellets by blowing.
- 25

As depicted above, the pelletizing aid is present in the cooling medium. It can also be added to the hot melt composition prior to blending or during the pelletizing steps by cofeeding a solution of pelletizing aid with the hot melt composition.

30 As noted above, it is well known in the art that stabilizers or antioxidants can also be added to the compositions in small amounts and have no effect on the other physical properties of the compositions. Other compounds that could be

added that also do not effect physical properties are pigments for color, fluorescing agents, and any compounds that mask odor. Additives such as these are known to one of skill in the art.

This invention is further illustrated by the following non-limiting
5 examples.

EXAMPLES

Test Methods

10 1. Melt Viscosities

The melt viscosities of the hot melt adhesives were determined on a Brookfield Thermosel Viscosmeter Model DV-II+. using either a number 21 or 27 spindle.

15 2. Specific Gravity

The specific gravity was determined using test method ASTM D792 with isopropyl alcohol as the liquid.

3. Mettler Softening Point

20 The Mettler softening points are determincd using test method ASTM D3461.

4. Dynamic Temperature Steps

Storage modulus, G' , at 25°C and T_g were determined using a Rheometrics
25 Scientific Dynamic Mechanical Spectrometer Model # RDS7700. The parallel plates used had a 25 mm diameter and a 1.502 mm gap. The instrument was set to a frequency of 10 rads/sec and temperature sweep was performed from 180°C to -50°C.

30 5. Bloom Gelometer

Rigidity of the samples was determined using a Precision Bloom Gelometer Catalog No. 68705.

EXAMPLES 1-4

The following compositions are provided for illustrative purposes only.

5 These examples illustrate the physical properties achieved with these types
of hot melt compositions but there are many more compositions with differing
physical characteristics.

Examples 1 and 2 illustrate the invention using only a high molecular
weight block substantially linear A-B-A block copolymer. Examples 3 and 4
illustrate the use of a blend of a high molecular weight block copolymer and
10 another block copolymer. These examples illustrate compositions that are useful
for molded articles. The dynamic temperature steps are especially illustrative of
this. See exhibit no. 1.

TABLE I
Composition By Weight Percent

Example	1	2	3	4
Kraton G1651	10.0	5.0	7.0	7.0
Kraton G1650		5.0	12.0	17.0
Kaydol Oil	89.5	89.5	80.0	75.0
*Antioxidant	0.1	0.1	1.0	0.5
**UV Absorber	0.4	0.4		0.5
***Pigment		Minute Amount	Minute Amount	
About 0.1% Shamrock S-395 Pelletizing aid was added to each of the compositions.				
• Either Irganox 1076 antioxidant or Irganox 1010 antioxidant or a blend of the two may be used.				
** A blend of approximately half Tinuvin 770 and half Tinuvin 328 was used.				
***Minute amounts of either Sudan Blue 670, Sudan Orange 220, or Sudan Yellow 146 or blends thereof may be used.				

Table 2
Physical Characteristics

Example	1	2	3	4
Method Used				
Specific Gravity	0.86	0.85	0.86	0.86
Density (#/gal)	7.1	7.1	7.1	7.2
Viscosity @ 325°F	143,250 cp	1,770 cp		
Viscosity @ 350°F	21,625 cp	770 cp		
Viscosity @ 375°F	4,350 cp	190 cp		
Viscosity @ 400°F	1,060 cp	60 cp		
Mettler Soften Pt (°F)	282.8 ± 2.9	255.8 ± 0.3		
G' at 300°F	2.64E+04	3.29E+03	4.24E+03	4.18E+04
G' at 200°F	4.76E+04	1.97E+04	5.11E+04	2.11E+05
G' at 77°F	4.27E+04	3.12E+04	1.71E+05	5.14E+05
Tg(upper)-°C(°F)			97.9(208.2)	104.9(220.8)
Tg(lower)-°C(°F)	-58.1(-72.6)	-55.5(-67.9)	-54.3(-65.7)	-56.9(-70.4)

Examples 5 and 6 and Comparative Example A

5 Examples 5 and 6 illustrate compositions which may be used as hot melt pressure sensitive adhesives. Comparative example A is an example of a composition where G' falls outside the parameters specified for a hot melt pressure sensitive composition. From Table 4 it can be seen that it is necessary to raise the temperature to nearly 100°C for G' to fall within the pressure sensitive range.

Table 3
Composition By Weight Percent

	5	6	A
Kraton D4433-X (Linear SIS)	45.0		
Europrene Sol T190 (Linear SIS)		50.0	
Kraton D-1184 (Radial SBS)			50.0
Zonester 100	20.0		
Escorez 1310LC	35.0		
Wingtack Extra		50.0	
Zonatac 105			50.0
Antioxidant	0.2	0.2	0.2
About 0.1% Shamrock S-395 Pelletizing Aid was added to each of the Compositions.			
Antioxidant Irganox 1010, hindered phenolic antioxidant.			

Table 4

Rheology Data

G' @ (dynes/cm ²)	Example 5	Example 6	Comparative A
(77°F)25°C	9.0 x 10 ³	1.4 x 10 ⁶	8.3 x 10 ⁶
(100°F)38°C	6.5 x 10 ³	1.1 x 10 ⁶	6.9 x 10 ⁶
(200°F)93°C	3.0 x 10 ³	4.5 x 10 ³	2.7 x 10 ⁶
(300°F)149°C	1.1 x 10 ³		7.5 x 10 ³
Tg (°C)	8	4	-7.0

Claims:

- I. A polymeric composition in pellet form, comprising:
 - I. From about 97% by weight to about 99.9% by weight of a tacky hot melt composition, comprising:
 - a) from about 5% by weight to about 90% by weight of a thermoplastic polymer;
 - b) from about 0% by weight to about 65% by weight of a tackifying resin;
 - c) from about 0% to about 50% by weight of a plasticizer; and
 - d) up to about 2% by weight of an antioxidant; and
 - II. From about 0.1% by weight to about 3% by weight of a pelletizing aid, wherein the tacky hot melt composition comprises some minimum amount of tackifier, plasticizer or both, and is a pressure sensitive adhesive having a storage modulus, G' , at about 25°C, of less than about 5×10^6 dynes/cm², and each pellet has a substantially tack-free surface.
2. A polymeric composition in pellet form comprising:
 - I. From about 97% by weight to about 99.9% by weight of a tacky hot melt composition, comprising:
 - a) from about 2% by weight to about 20% by weight of a high molecular weight block copolymer having the general configuration A-B-A and a weight average molecular weight greater than about 200,000;
 - b) from about 20% by weight to about 98% by weight of a compatible plasticizer;
 - c) from about 0% to about 30% by weight of a compatible polymer; and
 - II. From about 0.1% by weight to about 3% by weight of a pelletizing aid, wherein the polymeric composition has a tack-free surface prior to melting the pellets, and after melting and resolidification.

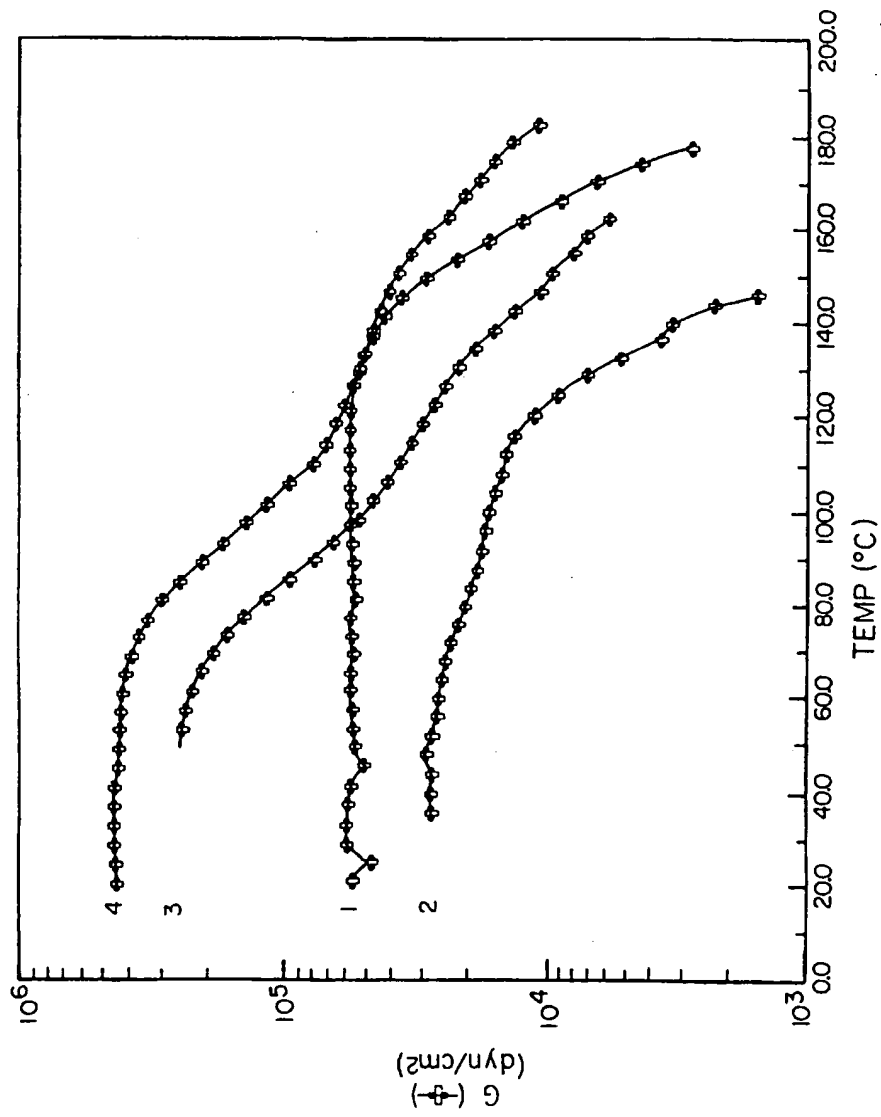
3. An article molded from a polymeric composition in pellet form wherein said polymeric composition in pellet form, comprises:
 - I. A tacky hot melt composition, comprising:
 - a) at least one high molecular weight triblock copolymer of the general configuration A-B-A; and
 - b) a plasticizer; and
 - II. A pelletizing aid,
wherein said pelletizing aid substantially surrounds the tacky composition such that the molded articles are soft, non-blocking and have a substantially tack-free surface.
4. A method for pelletizing the polymeric composition of any of Claims 1-2 comprising the steps of:
 - a) blending the hot melt components to form a substantially homogeneous mixture;
 - b) forcing said substantially homogeneous mixture through a die for forming substantially homogeneous ribbons and forming resultant pellets therefrom;
 - c) solidifying said pellets by use of a cooling medium; and
 - d) applying said pelletizing aid at some point during the pelletizing process.
5. A method for pelletizing the polymeric composition of any of Claims 1-2 comprising:
 - a) blending the hot melt components to form a substantially homogeneous mixture;
 - b) forcing said substantially homogeneous mixture through a die having a series of voids in a circular pattern to form a series of substantially homogeneous ribbons;
 - c) forcing said homogeneous ribbons past rotating blades in substantially parallel position to said die to form pellets;
 - d) substantially solidifying said pellets using a liquid cooling medium containing a pelletizing aid, said cooling medium being circulated past

said die and rotating blades on the side where said substantially homogeneous ribbons emerge;

- e) transporting said pellets to a drying area; and
 - f) substantially removing liquid from said pellets by blowing.
6. The polymeric composition of any of Claims 1-5 wherein said thermoplastic is a styrenic block copolymer having a styrene content from about 10% by weight to about 50% by weight and isoprene, butadiene, ethylene/butylene and ethylene/propylene midblocks and a diblock content of less than about 90%.
 7. The polymeric composition of any of Claims 1-5 wherein the thermoplastic polymer is selected from the group consisting of A-B-A triblock copolymer, A-B diblock copolymers, A-B-A-B-A-B multiblock copolymers, radial block copolymers, and grafted versions thereof; homopolymers, copolymers and terpolymers of ethylene; homopolymers, copolymers and terpolymers of propylene; and mixtures thereof.
 8. The polymeric composition of Claim 7 wherein said thermoplastic polymer is a homogeneous, substantially linear ethylene alpha olefin.
 9. The polymeric composition of any of Claims 1-5 wherein the tackifying resin is selected from the group consisting of aliphatic, cycloaliphatic and aromatic hydrocarbons and modified hydrocarbons and hydrogenated derivatives; terpenes and modified terpenes and hydrogenated derivatives; and rosins and modified rosins and hydrogenated derivatives; and mixtures thereof.
 10. The polymeric composition of any of Claims 1-5 wherein the plasticizer is selected from the group consisting of mineral based hydrocarbon oils, petroleum based hydrocarbon oils, polybutene, polyisobutylene, liquid tackifying resin, liquid elastomers, functionalized oils, fatty oils and mixtures thereof.
 11. The polymeric composition of any of Claims 1-5 wherein the pelletizing aid is selected from the group consisting of polyethylene waxes, modified polyethylene waxes, polyamide waxes and stearamide waxes and mixtures thereof.
 12. The polymeric composition of any of Claims 1-5 wherein the pelletizing aid is a polyethylene wax.

13. The polymeric composition of Claim 12 wherein the pelletizing aid is in powder form.
14. The method of any of Claims 4-5 wherein the blending step is carried out by means of a twin screw extruder.
15. The method of Claim 4 wherein the pelletizing aid is introduced in a manner selected from the group consisting of during the blending step, in the cooling medium and after solidification of the pellets and combinations thereof.
16. The polymeric composition of any of Claims 2-3 wherein the compatible polymer is selected from the group consisting of A-B-A triblock copolymers, A-B diblock copolymers, A-B-A-B-A-B multiblock copolymers, radial block copolymers and grafted versions thereof.
17. The polymeric composition of Claim 16 wherein the B block is selected from the group consisting of ethylene-propylene, ethylene-butylene and mixtures thereof.
18. The polymeric composition of Claim 17 wherein the A block is polystyrene.
19. The polymeric composition of any of claims 2-3 comprising a blend of between about 5% by weight and about 20% by weight of a high molecular weight block copolymer having the general configuration A-B-A, said block copolymer having polystyrene end blocks and a molecular weight greater than about 200,000; a compatible block copolymer of less than about 30% by weight; between about 50% by weight and about 95% by weight of a compatible plasticizer; and between about 0.01% by weight and about 0.6% by weight of a pelletizing aid comprising a polyethylene wax.
20. Molded article of Claim 3 wherein said article is selected from the group consisting of drum pads, shoe soles, therapeutic hand exercising grips, shock absorbers, acoustical insulators, pads for athletic gear, pads for medical equipment, furniture pads, bandages, burn victim bandages, synthetic skin and special effects articles.

Fig. 1



SUBSTITUTE SHEET (RULE 26)

Fig. 2

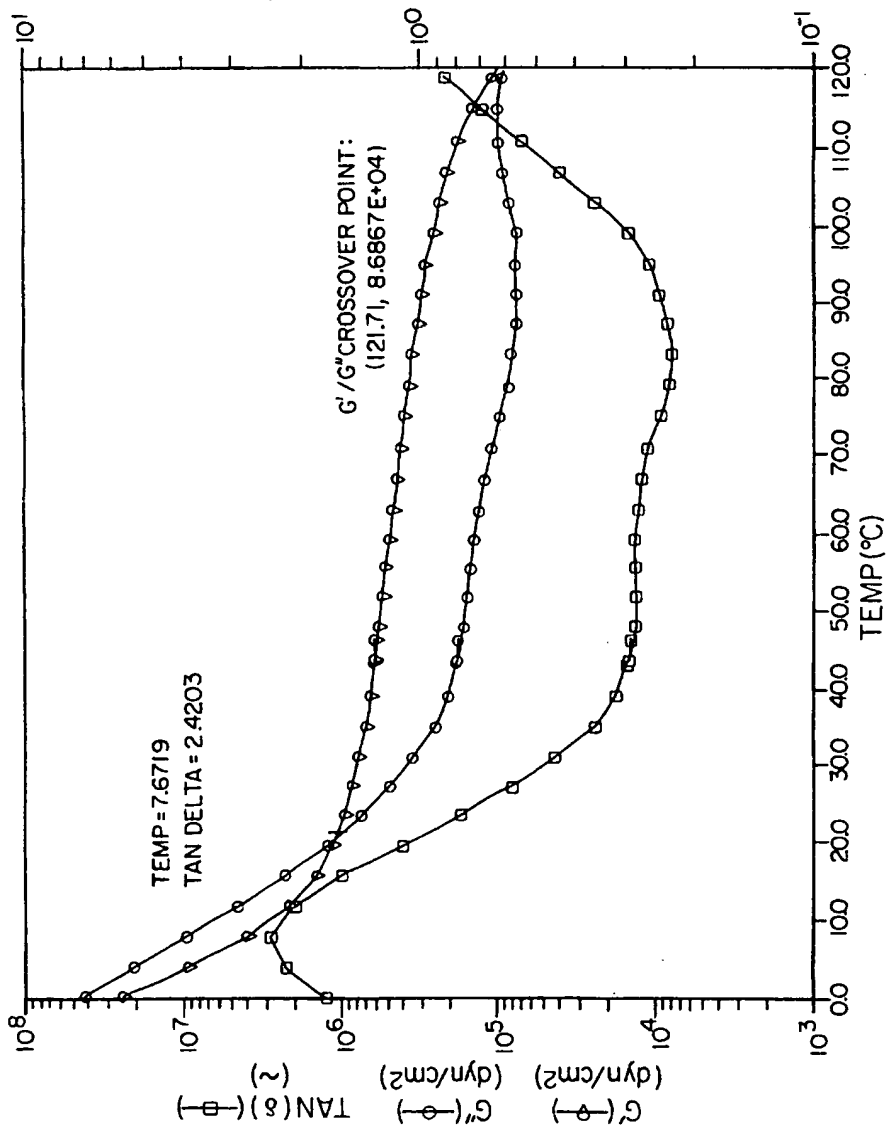


Fig. 3

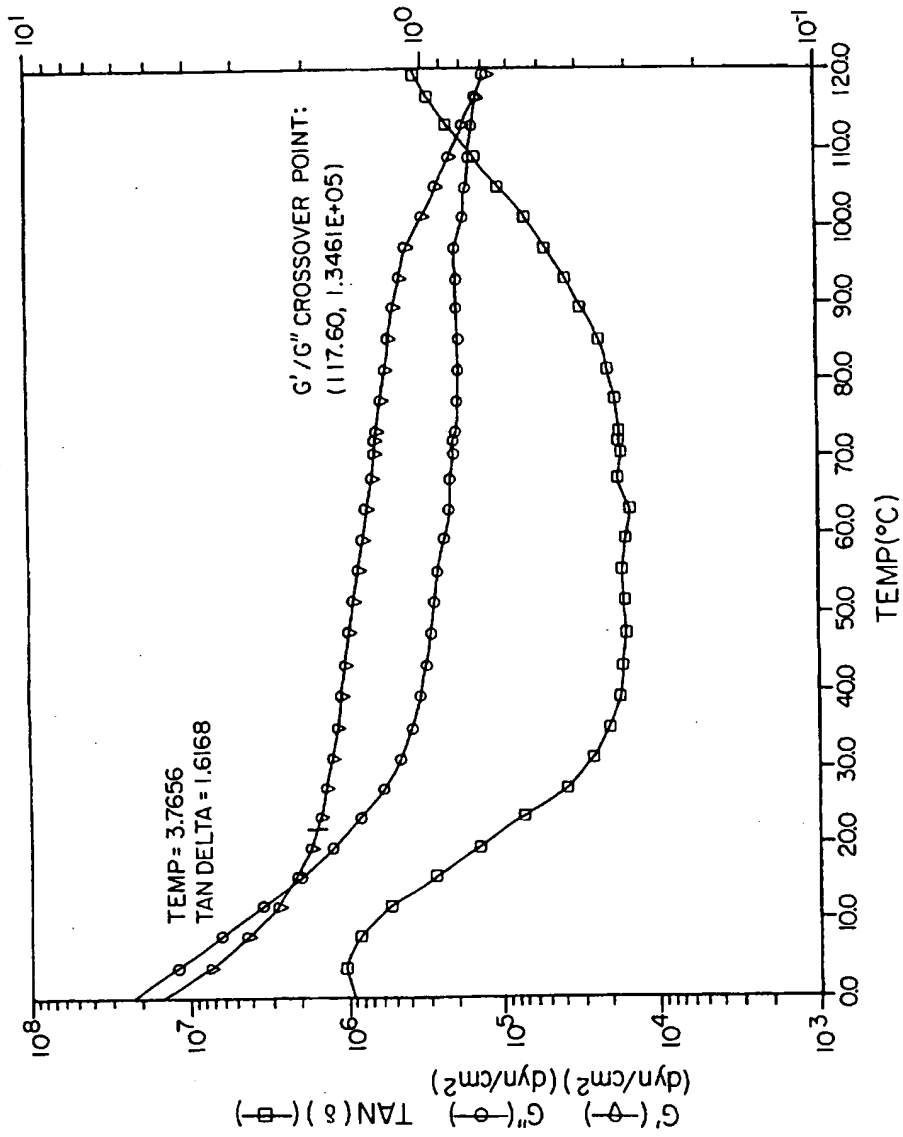
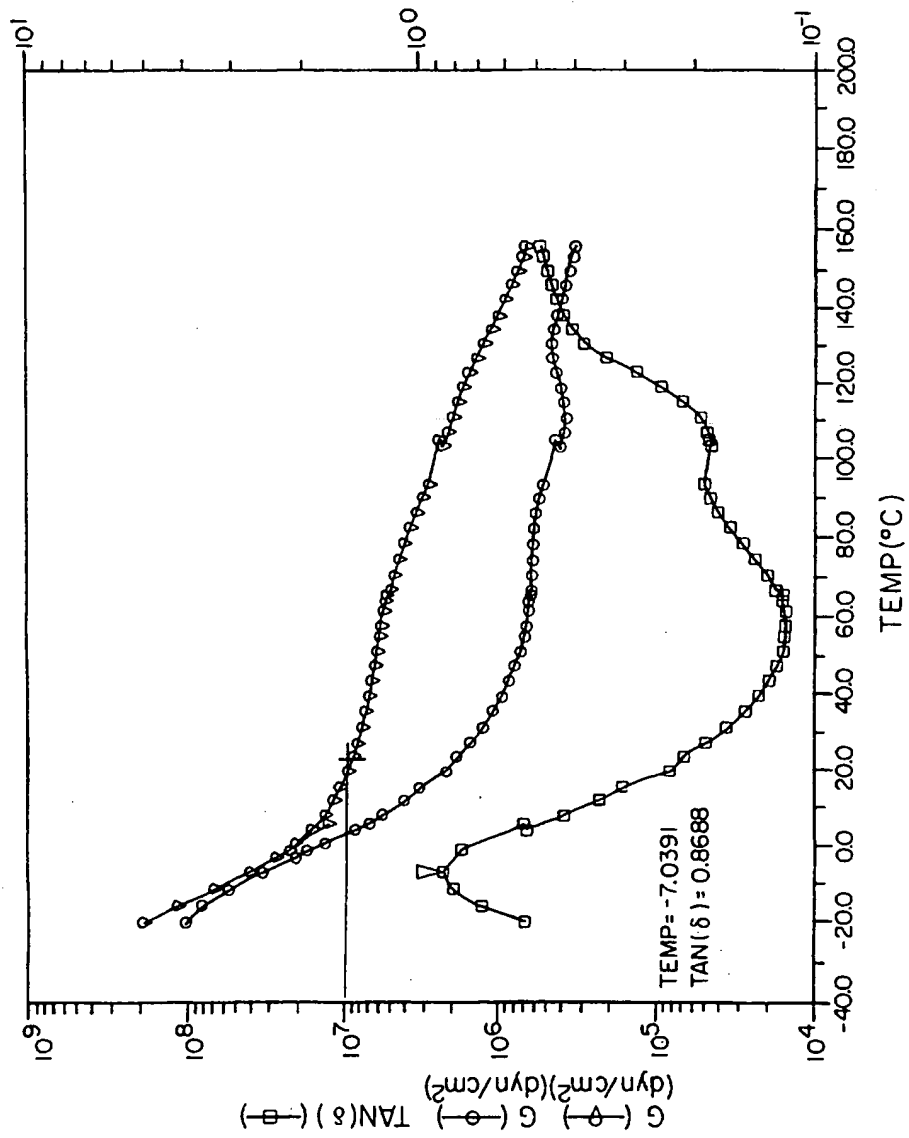


Fig. 4



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification⁶ : C08J 3/12, C09J 5/06</p>	<p>A3</p>	<p>(11) International Publication Number: WO 97/19582 (43) International Publication Date: 5 June 1997 (05.06.97)</p>
<p>(21) International Application Number: PCT/US96/18507 (22) International Filing Date: 18 November 1996 (18.11.96) (30) Priority Data: 08/559,006 16 November 1995 (16.11.95) US (71) Applicant: H.B. FULLER LICENSING & FINANCING, INC. [US/US]; 1200 Willow Lake Boulevard, St. Paul, MN 55110-5132 (US). (72) Inventors: SIMMONS, Eugene; 3440 Montmorency Street, Vadnais Heights, MN 55110 (US). SWEENEY, Kevin; 338 Wedgewood Drive, Mahtomedi, MN 55115 (US). LINDQUIST, Jeffrey; 9646 Indian Boulevard, Cottage Grove, MN 55016 (US). OLSON, Christopher; 5154 Parkside Drive, Paducah, KY 42001 (US). CARTES, Freddie; 1020 Wayside Drive, Paducah, KY 42003 (US). FARMER, James; 602 Newton, Johnston, IL 62951 (US). (74) Agents: STEINKRAUS, Walter, J. et al.; 1540 Kinnard Financial Center, 920 Second Avenue South, Minneapolis, MN 55402 (US).</p>	<p>(81) Designated States: AU, BR, CA, CN, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 3 July 1997 (03.07.97)</p>	
<p>(54) Title: A POLYMERIC COMPOSITION IN PELLET FORM (57) Abstract A polymeric composition in pellet form comprising a tacky hot melt composition, comprising a) from about 5 % by weight to about 90 % by weight of a thermoplastic polymer, b) from about 10 % by weight to about 65 % by weight of a tackifying resin, c) up to about 50 % by weight of a plasticizer, d) up to about 2 % by weight of an antioxidant, and a pelletizing aid, wherein the tacky hot melt composition is a pressure sensitive adhesive having a storage modulus, G', at about 25 °C, of less than about 5 x 10⁶ dynes/cm², and each pellet has a substantially tack-free surface. This invention further discloses a polymeric composition in pellet form suitable for molding articles. The composition comprises a tacky hot melt composition comprising at least one high molecular weight triblock copolymer of the general configuration A-B-A and a plasticizer and a pelletizing aid. The pelletizing aid substantially surrounds the tacky composition such that the molded articles are substantially free from surface tack. A method of forming the pellets is also disclosed.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

INTERNATIONAL SEARCH REPORT

International Application No

PC/US 96/18507

<p>A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C08J/12 C09J5/06</p>		
<p>According to International Patent Classification (IPC) or to both national classification and IPC</p>		
<p>B. FIELDS SEARCHED</p>		
<p>Minimum documentation searched (classification system followed by classification symbols) IPC 6 C08J</p>		
<p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched</p>		
<p>Electronic data base consulted during the international search (name of data base and, where practical, search terms used)</p>		
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p>		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>EP 0 115 307 A (NATIONAL STARCH AND CHEMICAL CORPORATION) 8 August 1984 see claims 1-8 see page 4, line 24 - page 5, line 4 see page 6, line 2 - page 7, line 13 see page 7, line 16-25; figures 1,2 see page 8, line 1 - page 9, line 12 see examples I,III ---</p>	<p>1-13,15, 19,20</p>
X	<p>EP 0 410 914 A (EASTMAN KODAK COMPANY) 30 January 1991 see claims 1-3,5,6,11,14,15 see example 6 ---</p>	<p>1,4,5, 7-9, 11-13,15</p>
X	<p>US 3 779 785 A (C.J.STILES ET AL.) 18 December 1973 see claims 1,5 ---</p>	<p>1,4,7,8</p>
<p>--- -/--</p>		
<p><input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.</p>		
<p>* Special categories of cited documents:</p>		
<p>'A' document defining the general state of the art which is not considered to be of particular relevance 'E' earlier document but published on or after the international filing date 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) 'O' document referring to an oral disclosure, use, exhibition or other means 'P' document published prior to the international filing date but later than the priority date claimed</p>		
<p>'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. '&' document member of the same patent family</p>		
<p>Date of the actual completion of the international search 13 May 1997</p>		<p>Date of mailing of the international search report 26.05.97</p>
<p>Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016</p>		<p>Authorized officer Hallemeesch, A</p>

2

INTERNATIONAL SEARCH REPORT

International Application No
PC1/US 96/18507

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 23823 A (EXXON CHEMICAL PATENTS INC.) 8 September 1995 see claims 6,8,9 ---	1,7,11
X	EP 0 575 900 A (BASF AKTIENGESELLSCHAFT) 29 December 1993 see claims 1-5 ---	1,7,8
X	GB 2 142 255 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 16 January 1985 see claims 1-7 see page 1, line 38 - page 2, line 2 ---	1,6,7,9, 11
P,X	WO 96 00747 A (NATIONAL STARCH AND CHEMICAL INVESTMENT HOLDING CORPORATION) 11 January 1996 see claim 1 see page 3, line 15 - page 6, line 6 see example 1 ----> The figure mentioned at page 3, lines 10-14, was not available at the time of the international search -----	1,4,6-15

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/18507

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0115307 A	08-08-84	AU 543796 B	02-05-85
		AU 2366784 A	02-08-84
		CA 1243569 A	25-10-88
		JP 59182871 A	17-10-84
		JP 63067822 B	27-12-88
EP 0410914 A	30-01-91	US 5041251 A	20-08-91
		CA 2064100 A,C	28-01-91
		DE 69008452 D	01-06-94
		DE 69008452 T	10-11-94
		EP 0484409 A	13-05-92
		ES 2051492 T	16-06-94
		WO 9101867 A	21-02-91
US 3779785 A	18-12-73	NONE	
WO 9523823 A	08-09-95	AU 1976295 A	18-09-95
		CA 2187107 A	08-09-95
		EP 0749454 A	27-12-96
EP 575900 A	29-12-93	DE 4316025 A	05-01-94
		DE 59305306 D	13-03-97
		ES 2096805 T	16-03-97
GB 2142255 A	16-01-85	US 4511696 A	16-04-85
WO 9600747 A	11-01-96	AU 2766695 A	25-01-96
		CA 2170752 A	11-01-96
		EP 0716667 A	19-06-96
		JP 9501735 T	18-02-97
		NO 960712 A	22-02-96